Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Isolation of EPR spectra and estimation of spin-states in two-component mixtures of paramagnets

Sonia Chabbra,[a] David M. Smith [b] and Bela E. Bode[a]*

[a]EaStCHEM School of Chemistry and Centre of Magnetic Resonance, University of St Andrews, St Andrews, Fife, KY16 9ST, Scotland, UK

[b]Sasol UK Ltd, St Andrews, Fife, KY16 9ST, Scotland, UK

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Mass Spectrometry Data

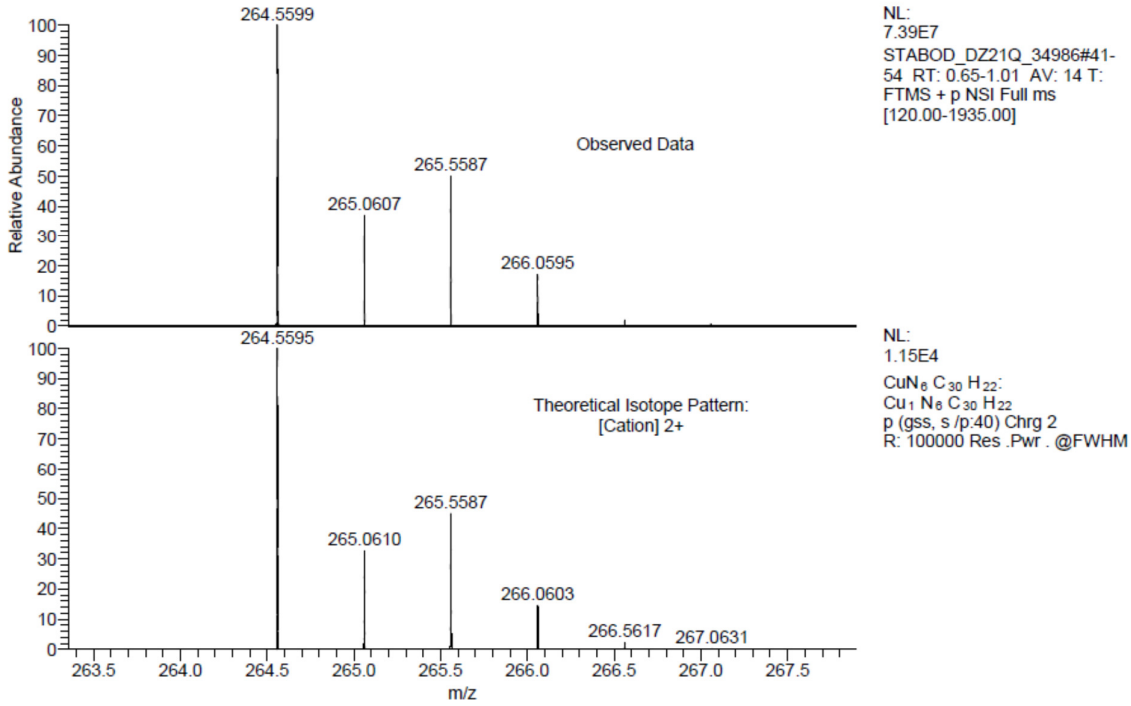

Figure S1 Mass spectrum of **3**

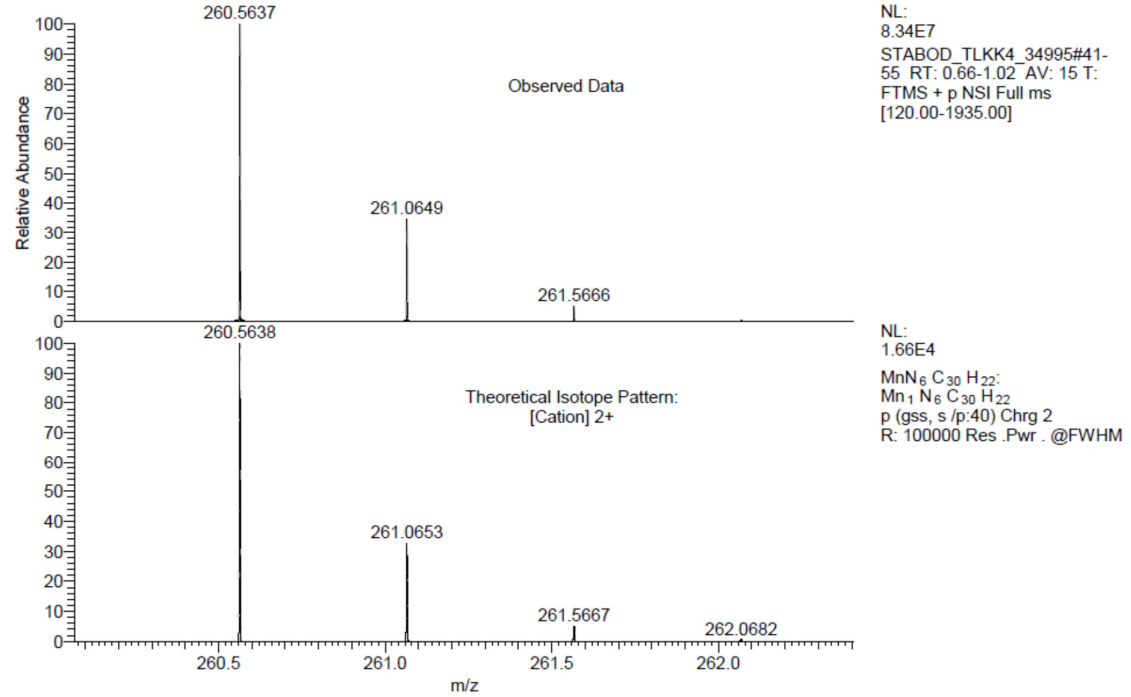

Figure S2 Mass spectrum of **4**

EPR Sample Preparation

TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) was obtained from Acros Organics. The triarylmethyl radical was a generous gift from the research group of Prof. Snorri Sigurdsson and prepared by standard procedures.[1] A 1 mM stock solution of TEMPO (7.8 mg, 50 μmol) in dry toluene was prepared and diluted by a factor of four to obtain a 250 μM solution. The same procedure was repeated to obtain 250 μM TEMPO in deuterated toluene (d8-toluene). 100 μL of these solutions were transferred to 4 mm EPR tubes. Furthermore, 50 μL of a 250 μM solution in toluene were transferred to a 4 mm EPR tube and 75 μL were transferred to a 3 mm EPR tube. A 1 mM solution of triarylmethyl radical (1 mg, 0.9 μmol) was prepared in toluene and 100 μL were transferred into a 4 mm EPR tube. All these samples were measured at X-band frequencies.

EPR Measurements

The inversion recovery experiment was performed at various field positions for both compounds **3** and **4** at Q-band (~34 GHz) at 10 K as shown in Figure S3. The traces were phase corrected and fitted with biexponential decay functions. The faster component is attributed to spectral diffusion and the slower component is to T_1 relaxation. The spectral diffusion has been neglected as its amplitude is an order of magnitude lower than the T_1 contribution. The T_1 time constant varies around 18% for compound **3** and 3% for compound **4** as shown in the Table S1 Furthermore, the zero-crossing point or the filter time T_F were read out from the individual traces and tabulated in Table S1. T_F varies about 14% for **3** and 22% for **4** across the field positions.

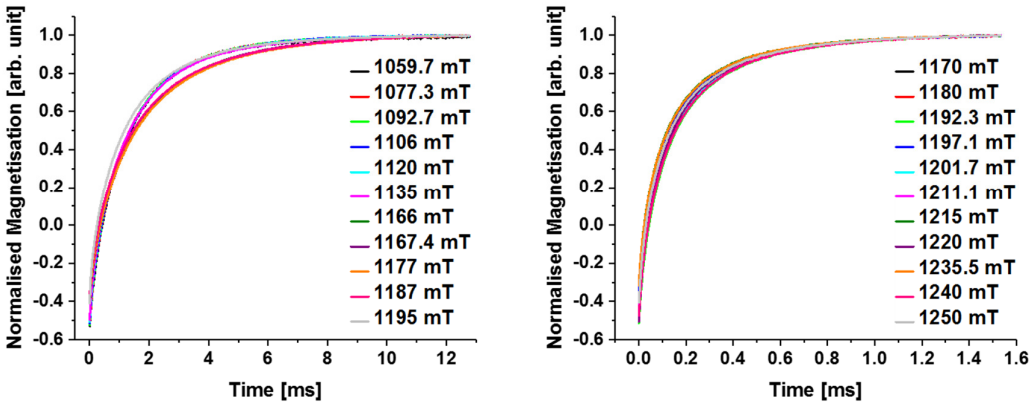

Figure S3 The inversion recovery traces recorded at different field positions for both compounds **3** (left) and **4** (right) measured at Q-band (~34 GHz) at 10 K.

Table S1 The longitudinal relaxation time constant, T_1 and filter time T_F obtained from inversion recovery traces (as shown in Figure S3)

Compound **3**			Compound **4**		
Field Positions [mT]	T_1 [ms]	T_F [µs]	Field Positions [mT]	T_1 [ms]	T_F [µs]
1059.7	1.78	420	1170	0.27	31
1077.3	1.80	409	1180	0.27	32
1092.7	1.80	402	1192.3	0.29	43
1106	1.85	399	1197.1	0.27	25
1120	1.84	378	1201.7	0.28	38
1135	1.88	366	1211.1	0.28	36
1166	2.39	356	1215	0.27	23
1167.4	2.37	359	1220	0.27	40
1177	2.44	349	1235.5	0.27	23
1187	2.45	304	1240	0.29	41
1195	1.89	244	1250	0.27	30

Echo detected field sweep experiments were performed on the mixture of **1** and **2** by optimising the echo forming pulses in the Cr(I) (**1**) or Cr(III) (**2**) spectra ($D_{Cr(I)}$ or $D_{Cr(III)}$), respectively. The spectrum obtained from $D_{Cr(III)}$ was used in combination with optimal inversion pulses and corresponding filter times to recover individual spectra of **1** and **2** from their mixture as shown in Figure S4.

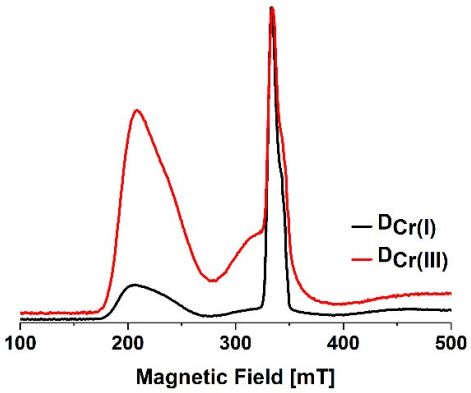

Figure S4 Echo detected field sweep experiment performed on the mixture of **1** and **2** by optimising the detection pulses ($D_{Cr(I)}$ or $D_{Cr(III)}$).

In order to demonstrate the effect of various experimental parameters a solution of a well-studied S = 1/2 TEMPO radical was used. The time domain traces were independent of the detection pulse length, T and deuteration of the solvent. However, sample size influences the nutation profile as shown in Figure S5. To obtain the nutation frequencies, the time domain data was background corrected followed by applying hamming window function, zero filling and Fourier transformation. The contributions from a second frequency diminish with a decrease in sample width instead of sample height (Figure S6). Nevertheless, the comparison of initial frequencies is reliable for a range of known S = 1/2 complexes as demonstrated in the Figure S7. The appearance of a second frequency (~14 MHz at X-band) is independent of deuteration of the solvent or experimental parameters discussed above. Hence, this contribution could be tentatively attributed to the protons present in the compound.

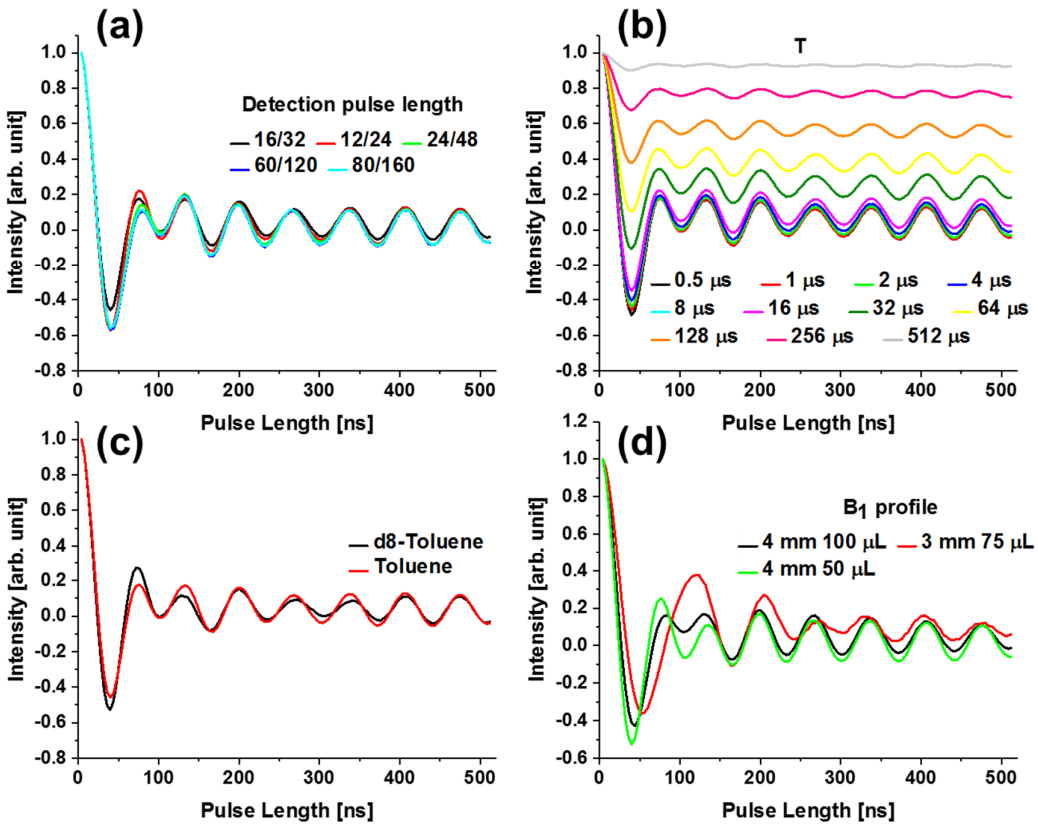

Figure S5 The time domain data obtained from the transient nutation experiments on TEMPO measured at the field position with maximum signal. All measurements were performed under identical conditions unless mentioned otherwise. Time domain traces were independent of the variation of (a) detection pulse length (b) T and (c) deuteration of solvent. Sample size affects the oscillation frequencies in time domain traces.

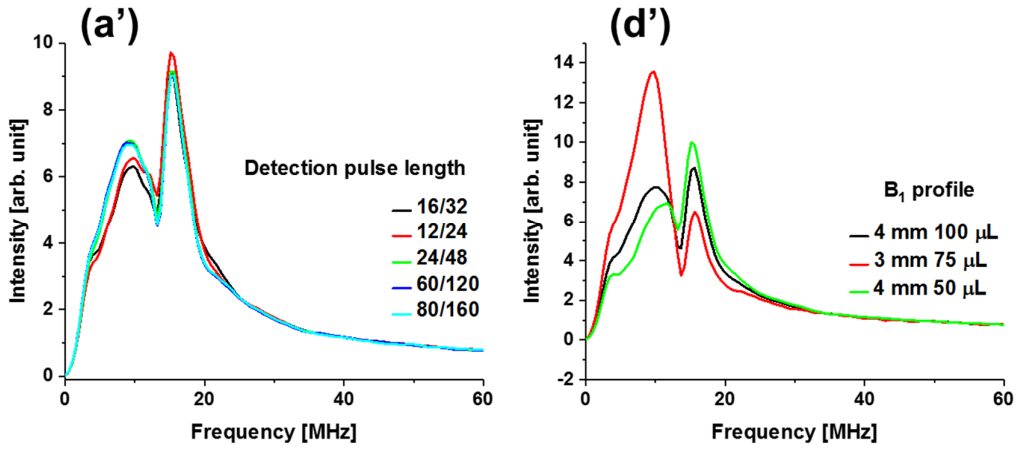

Figure S6 The Fourier transform of (a) and (d) from Figure S5. For $S = 1/2$ system, Nutation frequencies were observed to be 9 MHz. The second contribution seems to decrease by decreasing the sample width instead of sample height.

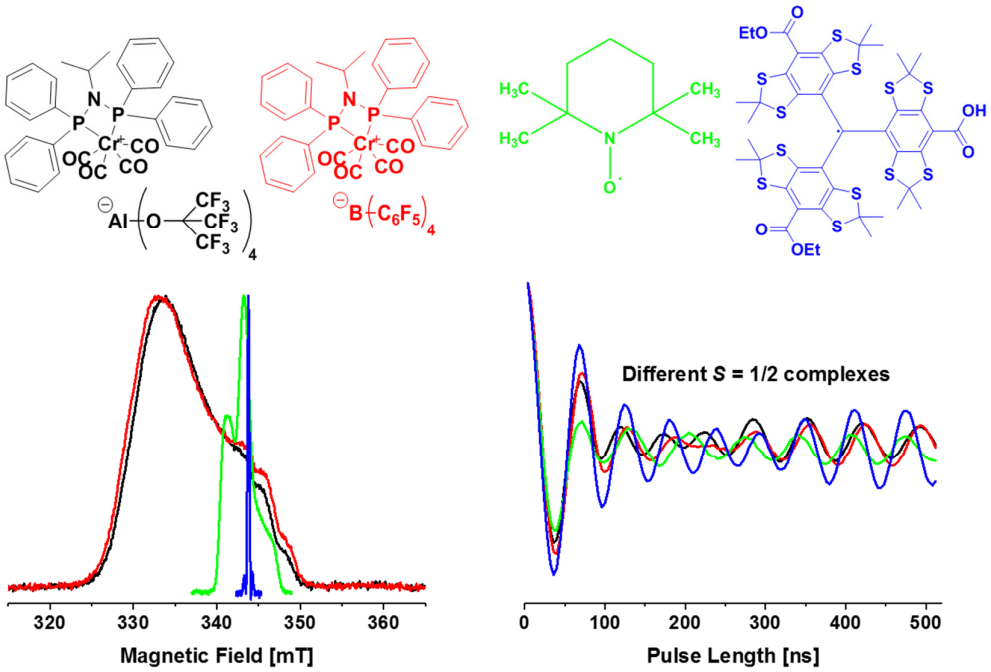

Figure S7 The echo detected field sweep (left) and time domain traces from transient nutation experiment (right) are shown for different S = 1/2 species. The position of first minima and maxima of transient nutation traces coincides for all the four complexes.

Calculated Nutation Frequencies

Equation 2 (main text) allows to straightforwardly predict the nutation frequency for the central (m_s = -1/2 and m_s = +1/2) transition for systems with a total electron spin of 1/2, 3/2 and 5/2 as relevant here:

$$\omega_{nut}(S, m_S, m_S + 1) = \omega_1\sqrt{S(S+1) - m_s(m_s+1)} \quad \text{(S1)}$$

$$\omega_{nut}\left({}^1/_2, m_S, m_S + 1\right) = \omega_1\sqrt{{}^3/_4 + {}^1/_4} = \omega_1 \quad \text{(S2)}$$

$$\omega_{nut}\left({}^3/_2, m_S, m_S + 1\right) = \omega_1\sqrt{{}^{15}/_4 + {}^1/_4} = 2\omega_1 \quad \text{(S3)}$$

$$\omega_{nut}\left({}^5/_2, m_S, m_S + 1\right) = \omega_1\sqrt{{}^{35}/_4 + {}^1/_4} = 3\omega_1 \quad \text{(S4)}$$

It follows that the nutation frequencies expected for the central transition for S = 1/2, 3/2 and 5/2 systems scale by a ratio of 1:2:3. Estimating the first minimum as half-frequency of the nutation curve the pulse lengths to achieve this inversion scale inversely (i.e. 3:2:1)

References

1. T. J. Reddy, T. Iwama, H. J. Halpern and V. H. Rawal, *J. Org. Chem.*, 2002, **67**, 4635-4639.